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Temperature dependence of the viscosity of highly starch-filled poly(hydroxy ester ether) biodegradable composites

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Abstract The temperature dependence of the viscosity of starch-filled poly(hydroxy ester ether) (PHEE) biodegradable composites was analyzed using Arrhenius and WLF equations. Corn starch/PHEE materials were extruded using a twin screw extruder with starch volume fractions from 0.27 to 0.66. Dynamic strain sweep measurements were carried out at 10 rad/s at six different temperatures from 100 °C to 150 °C. Both Arrhenius and WLF equations model equally well the temperature effect on viscosity of PHEE and starch/PHEE composites with starch volume fractions up to 0.36. Arrhenius equation with stress correction describes the stress dependence of viscosity of starch/PHEE composites with higher starch volume fractions. The activation energy using both Arrhenius equation and Arrhenius equation with stress correction is 62.7 kJ/mol for pure PHEE and starch/PHEE composites.

Key words Temperature · Viscosity · Composite · Activation energy · Starch · Biodegradable · Polyester

Introduction

Fillers have been extensively used in polymeric materials for several decades (Wypych 1993). Mainly as cost dilution additives, fillers are also added to polymeric materials for improvements of mechanical, electrical, and electromagnetic properties. For this reason, most filler materials are inorganic materials such as carbonates, silicates, sulfates, carbon, oxides, and metal powders/fibers (Shenoy et al. 1983). In recent years, starches, as low cost and renewable resources, have been widely used as fillers in the development of biodegradable polymer products (Willett 1994; Vaidya and Bhattacharya 1994; Kotnis et al. 1995; Koenig and Huang 1995; Willett and O'Brien 1997; Bastioli 1998; Willett et al. 1998; Ratto et al. 1999).

Most of the research published describes the processing and mechanical properties of the starch/biodegradable polymer composites. While reports on the rheology of filled suspensions are numerous, published work on the rheology of starch/biodegradable polymer composites is scarce. An understanding of the flow behavior (rheology) of the starch/polymer composites is essential for proper equipment design, and process and quality control. This research investigates the temperature dependence of the viscosity of starch-filled poly(hydroxy ester ether) (PHEE) composites.

Experimental

Materials

The materials used in this study and their physical properties are listed in Table 1. Cornstarch (Buffalo 3401) was used as the filler material. The starch was assayed for total carbohydrate by the phenol-sulfuric acid procedure (Dubois et al. 1956) and for

Table 1 Materials and their physical properties

	Corn starch wt %/vol. fraction	PHEE wt %/vol. fraction	Moisture content %
Density, kg/m³ (×10⁻³)	1.40	1.18	–
Extruded pellets 1	30/0.27	70/0.73	0.79
Extruded pellets 2	40/0.36	60/0.64	1.09
Extruded pellets 3	50/0.46	50/0.54	1.36
Extruded pellets 4	60/0.56	40/0.44	1.59
Extruded pellets 5	70/0.66	30/0.34	1.80

amylose by an amylose-iodine procedure (Knutson 1986). The level of carbohydrate in the starch sample is 95.63%; and the level of amylose in the carbohydrate is 21.51%. The surface area averaged diameter of starch granules is 14.1 μm and the volume averaged diameter is 16.1 μm measured using a Coulter Multisizer.

To minimize the water effect on the extrusion process and rheology of starch/polymer composites, the starch was dried before processing. Starch was dried in a forced air oven at 105 °C for 5 days, followed by 2 days in a vacuum oven also at 105 °C. The moisture content (MC) of the dried starch was 0.7% measured with an Ohaus Moisture Analyzer.

Poly(hydroxy ester ether) (PHEE) from Dow Chemical Company (Mang and White, 1992) was used as received. The glass transition temperature (T_g) of pure PHEE is 37 °C at an MC of 1.17% which is in equilibrium with the environment with a relative humidity (RH) of 50% and at 23 °C ($T_{g,dry}$ = 45 °C). The biodegradable (Mang et al. 1997; Rick et al. 1998) PHEE is derived from the reaction of bisphenol A diglycidyl ether with adipic acid.

The dried starch and PHEE were extruded using an 18-mm Leistritz twin screw extruder, operating at 100 rpm and temperatures from 120 °C to 165 °C, with starch weight percentage from 30% to 70%, the corresponding volume fractions from 0.27 to 0.66. Starch volume fractions are used in the following analysis. Before rheology measurements, the five batches of extruded pellets listed in Table 1 were put in double bags and sealed in a glass jar in a room with constant RH of 50% for two weeks. MCs of the pellets were measured before the rheology measurements and are listed in Table 1.

Rheology measurement

Dynamic strain sweep measurements were carried out using a strain-controlled ARES Rheometer Series IV (Rheometric Scientific) at 10 rad/s. The rheometer has two force balance transducers with torque measurement ranges from 0.2 g-cm to 200 g-cm and 2 g-cm to 2000 g-cm, respectively. In all measurements 25-mm parallel plates were used with a gap of 2 mm. In rheology measurements, cone-plate is frequently used because cone-plate is believed to give better adhesion between metal fixtures and a testing sample, and to keep constant shear rate across the measuring area. For a composite with starch as the filler, cone-plate cannot be used, since the average diameter of the cornstarch in this work is ~15 μm. The final gap in the center with cone-plate is 55.9 μm. This means that there are only about four layers of starch granules in the center, and wall effects on rheology measurements cannot be avoided if cone-plate is used.

Six temperatures from 100 °C to 150 °C were chosen for the extruded pellets with starch volume fraction from 0.27 to 0.46. Five temperatures from 100 °C to 140 °C were chosen for pure PHEE. Five temperatures from 110 °C to 150 °C were chosen for the pellets with starch volume fraction of 0.56 and four temperatures from 120 °C to 150 °C were chosen for the highest starch volume

fraction of 0.66. Temperature increment was always 10 °C. The lowest measuring temperature was kept at least 60 °C above the T_g of PHEE in the extruded pellets to obtain reliable melt rheology measurement. Experiments show that PHEE experiences cross-linking and possible re-polymerization at temperatures above 160 °C (data not shown), so all measurements were done below 160 °C.

Results and discussion

Experimental results

Figure 1 shows the complex viscosity of PHEE and starch/PHEE composites with starch volume fractions from 0.27 to 0.66 as a function of shear strain at the temperature of 110 °C and 130 °C, respectively.

Figure 1a, b shows clearly that pure PHEE displays a linear viscoelasticity in the measured strain range and at the two temperatures. Here linear viscoelasticity means
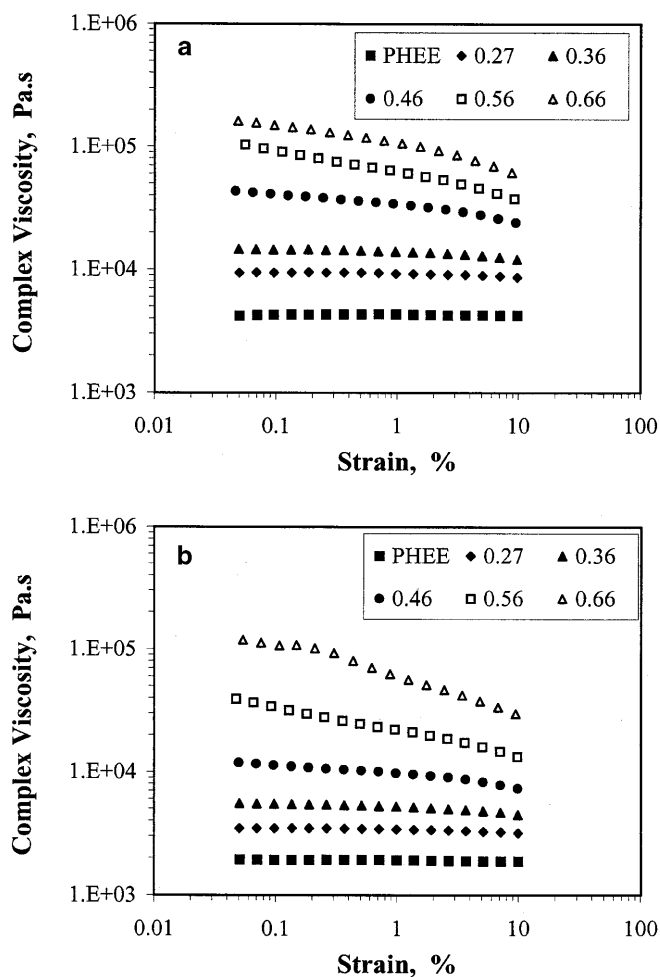
Fig. 1a, b Complex viscosity vs strain for PHEE and starch/PHEE composites with starch volume fraction from 0.27 to 0.66: **a** 110 °C; **b** 130 °C

that the viscosity does not change with strain (stress). This linear viscoelasticity is seen in the composite with starch volume fraction of 0.27. With the increasing starch concentration, starch/PHEE composites begin to display nonlinear viscoelastic behavior. For the composite with starch volume fraction of 0.36, up to 1% of strain, the viscoelasticity is still fairly linear. Above 1% of strain, the composite shows nonlinear viscoelasticity, though not significantly. At higher starch concentrations, the non-linear viscoelasticity of the composites is more pronounced. For the starch/PHEE composites with starch volume fraction of 0.46 and above, the rheological response becomes nonlinear over the entire strain range. The change of composite viscoelasticity from linear to nonlinear with the increase of starch volume fraction was found at all temperatures measured.

Temperature dependence of the composite viscosity

Numerous empirical equations have been proposed for correlating the effect of temperature on the viscosity of polymeric materials. In practice, the most frequently used equations are those proposed by Arrhenius (Mayadunne et al. 1996; Maiti and Mahapatro 1988; Saini et al. 1986; Ghosh and Maiti 1997) and Williams, Landel and Ferry (WLF) (Ferry 1961).

The Arrhenius equation takes the form

$$\eta_T = A \exp\left(\frac{E_a}{RT}\right) \tag{1}$$

where η_T is the viscosity of a polymeric material at a temperature, T (in degrees K), A is a constant, E_a is the activation energy for flow, and R is the universal gas constant.

From Eq. (1), a plot of $\ln(\eta_T)$ vs $1/T$ gives a straight line with a slope of E_a/R. Figure 2a–c show the plots of $\ln(\eta_T)$ vs $1/T$ at six strains (0.05–10%) for the starch/PHEE composites with starch volume fraction of 0.27, 0.46, and 0.66, respectively. Figure 2a shows that the plot of $\ln(\eta_T)$ vs $1/T$ is linear for the starch/PHEE composite with starch volume fraction of 0.27. Similar plots (data not shown) for pure PHEE and the starch/PHEE composite with starch volume fraction of 0.36 also show that the melt viscosity is still only a function of temperature. When starch volume fraction increases to 0.46, the composite viscosity becomes dependent on the strain (stress) (Fig. 2b). With a further increase in starch concentration, the composite viscosity is strongly dependent on stress besides the temperature (Fig. 2c). The regression parameters using the Arrhenius equation for PHEE and starch/PHEE composites with starch volume fraction up to 0.36 are listed in Table 2. For starch volume fraction of 0.36 and less, E_a is 62.7 (± 3.6) kJ/mol.
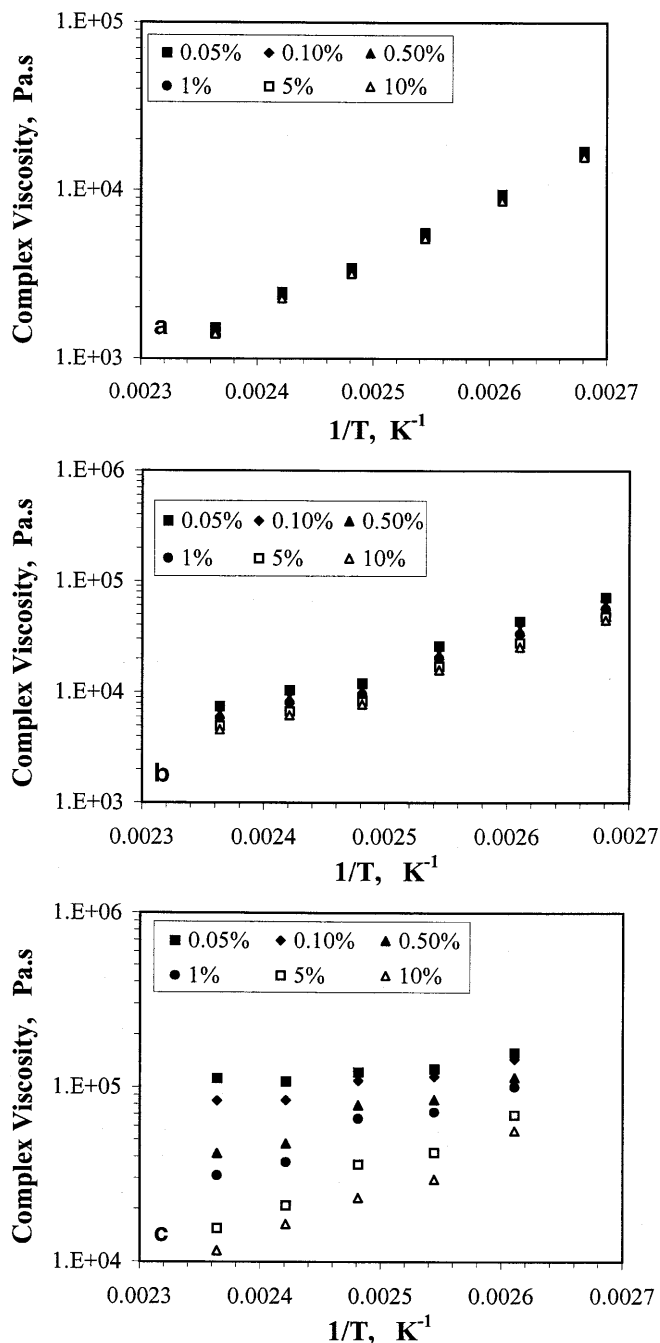

Fig. 2a–c Arrhenius plot of complex viscosity at different strains: a 0.27; b 0.46; c 0.66 (starch volume fraction)

The WLF equation is given by

$$\log\left(\frac{\eta_T}{\eta_0}\right) = \frac{-c_{1,0}(T - T_0)}{c_{2,0} + T - T_0} \tag{2}$$

where T_0 in degrees K is a reference temperature, and $c_{1,0}$ and $c_{2,0}$ are constants related to the reference temperature. By plotting $[(T - T_0)/\log(\frac{\eta_T}{\eta_0})]$ vs $(T - T_0)$,

**Table 2** Regression parameters in Arrhenius and WLF equations

Composite (starch vol. frac.)	Arrhenius (Eq. 1)		WLF (Eq. 2)			
	E_a (kJ/mol)	A (Pa.s) $\times 10^4$	$c_{1,0}$	$c_{2,0}$	T_0 °K	η_0 (Pa.s) $\times 10^{-3}$
PHEE	61.2	2.01	3.02	177	413	1.01
0.27	62.3	3.00	3.55	219	423	1.64
0.36	64.8	2.03	2.22	149	423	2.29
Average	62.7 ± 3.6	–	–	–	–	–

$c_{1,0}$ and $c_{2,0}$ can be determined. The regression parameters determined using the WLF equation for PHEE and starch/PHEE composites with starch volume fraction up to 0.36 are listed in Table 2. The highest measured temperature was chosen as the reference temperature for each composite.

Figure 3 shows the regression results using the Arrhenius and WLF equations compared with the measured data. Each measured data is an averaged value of viscosity at all strains at a temperature. In general, both models describe the experimental data ($R^2 \geq 0.99$).
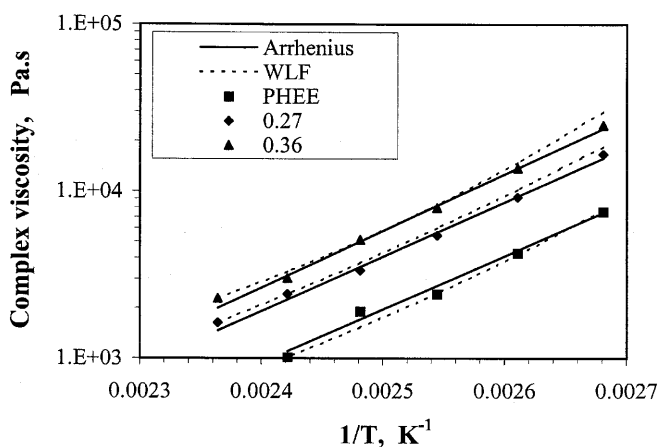
Fig. 3 Comparison of complex viscosity between measured values and those predicted by the Arrhenius and WLF equations (starch volume fraction ≤0.36)

Table 3 Regression parameters in Arrhenius equation with stress correction

Composite (starch vol. frac.)	E_a (kJ/mol)	η_0' (Pa.s) $\times 10^4$	V* (m³/mole)
0.46	62.7	1.14	0.568
0.56	62.7	2.19	0.301
0.66	62.7	8.41	0.686

◄
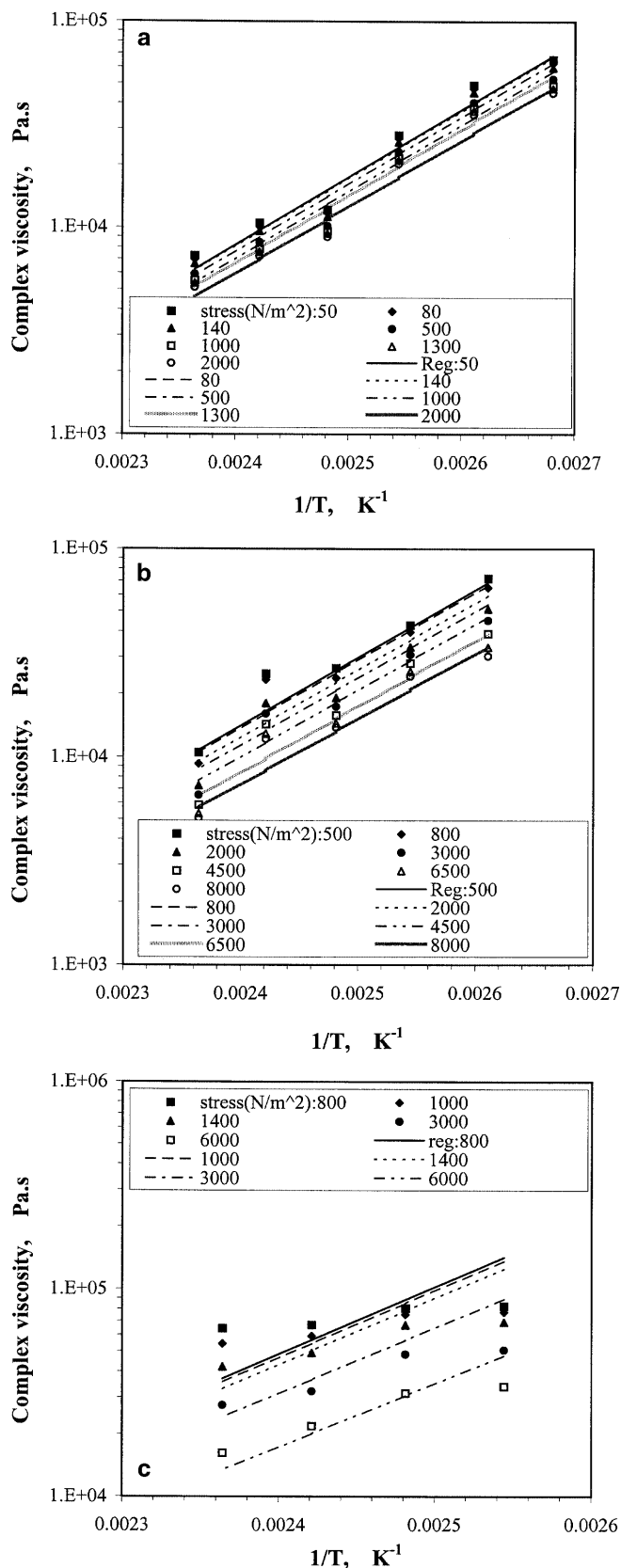
Fig. 4a–c Comparison of complex viscosity between the measured values and regression fit using the Arrhenius equation with stress correction: **a** 0.46; **b** 0.56; **c** 0.66 (starch volume fraction)

Stress dependence of the composite viscosity at high starch concentrations

For composites with starch volume fraction below 0.36, both the Arrhenius and WLF equations provide good descriptions of the experimental data. At higher starch volume fractions, the composite viscosity becomes stress dependent (Fig. 2b, c). Efforts were made to correlate the temperature dependence of composite viscosity at constant stresses using an Arrhenius equation modified to take into account the stress effect on the viscosity. The modified Arrhenius equation is called Arrhenius equation with stress correction in the following analysis and is expressed as (Ward and Hadley 1993)

$$\eta_{T} = \eta_{0}' \exp\left(\frac{E_{a} - \tau V^{*}}{RT}\right) \quad (3)$$

In this model, two constants need to be determined: η_{0}' the viscosity at zero shear stress, and V^{*} the activation volume. τ is the shear stress, which can be obtained directly from the experimental data. E_{a} is chosen as the activation energy averaged from the three E_{a}s of PHEE, and of composites with starch volume fractions of 0.27 and 0.36, which is 62.7 kJ/mol. By plotting $\ln(\eta_{T})$ vs τ/T at a fixed temperature and varying stresses, the intercept determines η_{0}', and the slope determines V^{*}. The regression parameters determined using Eq. (3) for the three composites with starch volume fraction of 0.46, 0.56 and 0.66 are listed in Table 3.

Figure 4 shows the comparison of composite viscosity between measured and regression using Eq. (3) at selected stresses for composites with starch volume fraction of 0.46, 0.56, and 0.66, respectively. Figure 4a, b shows good agreement between the experimental data and the regression fit. Though the agreement between the experimental data and the regression shown in Fig. 4c is not as good as that in Fig. 4a, b the regression displays correctly the trend the experimental data exhibit. It is noted that η_{0}' increases approximately exponentially with the increase of the starch volume fraction.

Conclusions

The temperature dependence of viscosity of PHEE and starch/PHEE composites has been characterized. Both the Arrhenius and WLF equations can be used to model the temperature effect on viscosity of PHEE and starch/PHEE composites with starch volume fractions up to 0.36. The Arrhenius equation with stress correction well describes the stress dependence of viscosity of starch/PHEE composites with higher starch volume fractions. The activation energy using both the Arrhenius equation and the Arrhenius equation with stress correction can be unified as 62.7 kJ/mol for pure PHEE and starch/PHEE composites.

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